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An idealized model for nonequilibrium dynamics in molecular systems

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The nonequilibrium dynamics of highly nonlinear and multidimensional systems can give rise to emergent chemical behavior which can often be tracked using low-dimensional order parameters such as a reaction path. Such behavior cannot be readily surmised by stationary projected stochastic representations such as those described by the Langevin equation or the generalized Langevin equation (GLE). The irreversible generalized Langevin equation (iGLE) contains a nonstationary friction kernel that in certain limits reduces to the GLE with space-dependent friction. For more general forms of the friction kernel, the iGLE was previously shown to be the projection of a mechanical system with a time-dependent Hamiltonian [R. Hernandez, J. Chem. Phys. **110**, 7701 (1999)]. In the present work, the corresponding open Hamiltonian system is shown to be amenable to numerical integration despite the presence of a nonlocal term. Simulations of this mechanical system further confirm that the time dependence of the observed total energy and the correlations of the solvent force are in precise agreement with the projected iGLE. This extended nonstationary Hamiltonian is thus amenable to the study of nonequilibrium bounds and fluctuation theorems.
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I. INTRODUCTION

One of the critical successes of statistical mechanics has been the connection it enables between easily computable equilibrium quantities and dynamical observables of nonequilibrium systems. When the latter are not too far from equilibrium, for example, linear-response theories work well. As systems increase in complexity, however, more general methods are needed to treat their nonequilibrium dynamics.[1,2] Moreover, such highly nonlinear problems can give rise to chemically interesting emergent behavior beyond the well-studied examples of phase transitions and self-assembly.[3–8] This, in part, has spurred a significant interest in exploring relations or constraints involving the free energies and fluctuations in nonequilibrium systems.[9–15]

While the nonequilibrium dynamics in complex materials may occur at very long length and time scales, many chemical processes therein occur at much shorter such scales. Thus, for chemically interesting problems, there is an advantage in separating the multiple time scale responses from the environment in contrast to those of the subsystem. Indeed, several successful models for chemical processes have separated the subsystem by treating the environment as a uniform solvent. For example, the dynamics of the chosen subsystem can be described by the Langevin or the generalized Langevin equation (GLE) insofar as the environment is assumed to be in a steady-state equilibrium throughout the dynamical event, vis-à-vis the linear responding bath is stationary and obeys a fluctuation-dissipation theorem.[16–30]

In many instances, the environment is not stationary, and as such a nonstationary version of the GLE would be desirable.[31–35] Examples of this include polymerization dynamics,[32,33] protein dynamics,[36,37] dynamics in supercritical fluids,[38] diffusion through anisotropic materials (liquid crystals),[39] and diffusion through swelling colloidal suspensions.[40,41] In each of these cases, a chosen projective coordinate associated with a given particle or localized set of particles evolves in a time-dependent environment which is either driven by external forces or self-consistently by the collective motion of all the chosen coordinates. Two relevant limits involve the motion of the projective coordinate when it is driven by a bare potential that is either that of a free particle or that of a trapped harmonic oscillator. In both cases, the solvent can effectively trap the particle, leading these limits to be more similar than what one would naively expect. This observation is well understood in the context of the famous problem of the frequency shift in the projection of the Zwanzig Hamiltonian to the Langevin equation.[29,42–44]

In principle, it is easy to write a nonstationary generalization of the GLE as

$$\dot{v} = -\int^{t} dt'\, \gamma(t,t')\, v(t') + \xi(t) + F(t), \tag{1a}$$

where $F(t)[\equiv -\nabla_q V(q(t))]$ is the external force, $v(=\dot{q})$ is the velocity, q is the mass-weighted position, $\xi(t)$ is the random force due to a solvent, and $\gamma(t,t')$ represents the nonstationary response of the solvent. To completely specify this system of equations, a closure connecting the random force to the friction kernel is needed. The fluctuation-dissipation relation (FDR) provides such a closure for the GLE when the thermal bath (solvent) is held at a constant temperature T.[22]

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An obvious generalization of the FDR for nonstationary friction kernels is the requirement

$$k_B T \gamma(t,t') = \langle \xi(t)\xi(t') \rangle. \tag{1b}$$

Unfortunately, such a construction will not necessarily be satisfied for an arbitrary nonstationary friction kernel, nor will it necessarily be associated with the dynamics of a higher-dimensional mechanical system.

The GLE model with space-dependent friction (xGLE) developed by Lindenberg and co-workers,[45,46] and Carmeli and Nitzan[47] does exhibit the structure of Eq. (1) and as such is an example of nonstationary stochastic dynamics. In recent works,[31–35] a generalization of this model was developed which includes arbitrary nonstationary changes in the strength of the friction, but like the xGLE model does not include changes in the response time. As such it is not quite the ultimately desired nonstationary GLE. Avoiding redundancy in the term "generalized GLE," the new formalism has been labeled the *irreversible* generalized Langevin equation (iGLE), thereby emphasizing the irreversibility, vis-à-vis nonstationarity, in the response of the quasiequilibrium environment. But this "irreversibility" may not necessarily persist at long times, and therefore Drozdov and Tucker chose to call such an equation of motion the multiple-time-scale generalized Langevin equation (MTSGLE) in their application of the iGLE to study local-density enhancements in supercritical fluids.[38]

Regardless, a major criticism of the iGLE has been its phenomenological form and the apparent lack of a microscopic connection. However, a microscopic model system in which the bath modes are explicit and whose projection is precisely given by the iGLE was constructed in Ref. 35. It provides a test bed for exploring nonequilibrium theorems as well as the signatures of emergent phenomenon at each of these scales. But the projection is approximate and might leave room for doubt as to its accuracy in the context of chemically relevant problems. To resolve this issue, the present work provides a clear methodology for integrating the nonlocal equations of motion of the mechanical system and uses this machinery to numerically verify that the mechanical system correctly projects to the putative nonstationary stochastic equation of motion.

The outline of the remainder of this paper is as follows. The iGLE model is first summarized in Sec. II, explicitly indicating the limit in which position-dependent friction may be recovered. In Ref. 35, it was shown that the iGLE may, indeed, be obtained as a projection of an open Hamiltonian system, in analogy with the similar construction for the GLE.[20,42,48–50] But that work left two possibly open questions: (1) Is the approximation ignoring the third-and higher-order correlations justified in this system as it is in the projection of the GLE? (2) What is the nature of the nonlocal term in the full-dimensional mechanical system? In Sec. II, the connections between the projection of the Hamiltonian of Ref. 35 onto a chosen dynamical variable and that obtained by the xGLE are further illustrated, and the possibly troubling nonlocal term it contains is also further explored. The results of several numerical simulations of the Hamiltonian system are presented in Sec. III in order to illustrate the effect of the nonlocal term on the dynamics and to verify that the constructed random force does obey the FDR.

II. THE iGLE AND SPACE-DEPENDENT FRICTION

A. Stochastic dynamics

The iGLE may be written as

$$\dot{v}(t) = -\int_0^t dt' g(t) g(t') \gamma_0(t-t') v(t') + g(t)\xi_0(t) + F(t), \tag{2}$$

where $g(t)$ characterizes the irreversibility in the equilibrium environment, and there exists a FDR between the Gaussian random force $\xi_0(t)$ and the stationary friction kernel $\gamma_0(t-t')$. Through the identities

$$\gamma(t,t') \equiv g(t) g(t') \gamma_0(t-t'), \tag{3a}$$

$$\xi(t) \equiv g(t)\xi_0(t), \tag{3b}$$

the iGLE is a construction of the nonstationary Eq. (1). One possible interpretation of the role of $g(t)$ in the iGLE is that it corresponds to the strength of the environmental response as the reactive system traverses the environment through an *a priori* specified trajectory, called, $y(t)$. Assuming that one also knows the field $f(y)$, which is the strength of the environmental friction over this configuration space, then the irreversibility may be written as

$$g(t) = f(y(t)). \tag{4}$$

In the case that the chosen coordinate is itself the configuration space over which the friction varies, i.e., $y=x$, the GLE with the space-dependent friction of Carmeli and Nitzan is formally recovered.[47]

But the iGLE is more general than the xGLE because it allows for a variety of "irreversible" time-dependent environments. For example, in the WiGLE model,[34] each particle, labeled by n, is in an environment induced by the average of the properties of itself and w neighbors,

$$g_n(t) \equiv \langle |R(t)| \rangle_n^{\xi}, \tag{5a}$$

$$\langle |R(t)| \rangle_n \equiv \frac{1}{w+1} \sum_{i \in S_{w,n}} |R_i(t)|, \tag{5b}$$

where $S_{w,n}$ is the set of w neighbors. In the limit that $w \to 0$, the chosen coordinate is dissipated only by a function of its position, which is precisely the limit of space-dependent friction. In the limit that $w \to \infty$, the chosen coordinate is instead dissipated by a macroscopic average of the motion of all the reacting systems in the sample. The contribution of a particular particle to this average is infinitesimally small, and hence the friction contains no space-dependent friction. In between these limits, there is a balance between self-dissipation due to a space-dependent friction term and heterogeneous dissipation due to the average of the motion of the w neighbors.

B. Mechanical systems

In recent work, a Hamiltonian has been obtained whose projection is the iGLE when $g(t)$ depends exclusively on time, i.e., it includes neither explicit space dependence nor the WiGLE dependence.[35] This so-called iGLE Hamiltonian may be written as

$$\mathcal{H}_{\mathrm{iGLE}} = \frac{1}{2}p_q^2 + \{V(q) + \delta V_1(q,t) + \delta V_2[q(\cdot),t]\} - g(t) \times \left[\sum_{i=1}^{N} c_i x_i\right] q + \sum_{i=1}^{N}\left[\frac{1}{2}p_i^2 + \frac{1}{2}\omega_i^2 x_i^2\right], \tag{6a}$$

where

$$\delta V_1(q,t) \equiv \frac{1}{2}g(t)^2 \sum_{i=1}^{N} \frac{c_i^2}{\omega_i^2} q^2, \tag{6b}$$

$$\delta V_2[q(\cdot),t] \equiv \frac{1}{2}\int_0^t dt' a(t,t')[q(t') - q(t)]^2 - \frac{1}{2}\left[\int_0^t dt' a(t,t')\right] q(t)^2, \tag{6c}$$

where

$$a(t,t') \equiv g(t)\dot{g}(t')\gamma_0(t-t'), \tag{6d}$$

and the time dependence in $q(t)$ is explicitly included in the definition of the $\delta V_2[q(\cdot),t]$ functional for clarity. Ignoring the δV_2 term and identifying g as in Eq. (4), this Hamiltonian is similar to the xGLE Hamiltonian for space-dependent friction. This result is not surprising in the sense that the iGLE has a similar generalized structure. However, the xGLE Hamiltonian gives rise to an additional dependence on q whereas the iGLE Hamiltonian gives rise to an additional dependence on time t. The projections are thus analogous but not exactly the same.

C. Equation of motion

The nonlocality in the $\delta V_2[q(\cdot),t]$ term does present some difficulties which are worth considering. In the absence of this term, the extremization of the action readily leads to the usual Hamilton equations. In general, the presence of the δV_2 term contributes to the time evolution of the momentum $\dot{p}$ by way of the functional derivative,

$$-\frac{\delta S_2}{\delta q(t)}, \tag{7}$$

where the contribution to the action due to δV_2 may be written as

$$S_2 \equiv \frac{1}{2}\int_0^T dt \int_0^t dt' a(t,t') q(t')^2 - \int_0^T dt \int_0^t dt' a(t,t') q(t) q(t'), \tag{8}$$

and T is the arbitrary final time to which the action is evaluated. A simple calculation readily leads to

$$-\frac{\delta S_2}{\delta q(t)} = \int_0^t dt' a(t,t') q(t') + \int_t^T dt' a(t,t')[q(t') - q(t)]. \tag{9}$$

The first term in the right-hand side precisely cancels the contribution due to the nonstationarity in the friction kernel. However, the remaining second term depends on the arbitrary final time T. Its presence cannot be physically correct because it leads to different dynamics depending on the choice of T. In the limit that T is near, though greater, than t, this term vanishes, however. This suggests that an additional approximation ignoring the second term, thereby eliminating the transient effects from a term that depends arbitrarily on T, is warranted. (And this is consistent with the Carmeli and Nitzan derivation in that they, too, need to remove transient terms.) Within this approximation, the projection in Ref. 35 then leads to the iGLE.

Yet another potential pitfall posed by the $\delta V_2[q(\cdot),t]$ term is that its explicit integration may be computationally expensive. This expense can be mitigated when the stationary friction kernel has an exponential form. In this case, the derivative, $\partial \delta V_2[q(\cdot),t]/\partial t$, can be calculated using the auxiliary variable z, where

$$\frac{\partial z}{\partial t} = \dot{g}(t)q(t) - \frac{1}{\tau}z(t). \tag{10}$$

The value of $\partial \delta V_2[q(\cdot),t]/\partial t$ can then be obtained at each time step,

$$\frac{\partial \delta V_2[q(\cdot),t]}{\partial t} = \gamma_0 g(t) z(t). \tag{11}$$

All of the results shown in this paper have been calculated using the integration of the auxiliary variable z because it is consequently formally equivalent to the explicit integration of Eq. (6c) while requiring fewer computing cycles.

Thus the projection of the iGLE Hamiltonian leading to the iGLE with a purely time-dependent friction is analogous (and complementary) to the Carmeli and Nitzan projection to a GLE with space-dependent friction. The construction of such a Hamiltonian for an iGLE with arbitrary nonstationary friction, as manifested in the WiGLE, is still an open problem. In Sec. III, the dynamics of the iGLE Hamiltonian is explored through numerical simulations in order to observe the degree of energy conservation, as it is affected by δV_2, and the correlation of the constructed forces.

III. NUMERICAL RESULTS

In this section, numerical simulations of the Hamiltonian equivalent of the iGLE are presented. It is shown that the inclusion of the nonlocal term, $\delta V_2[q(\cdot),t]$, known to be small in the quasiequilibrium regime, is actually necessary generally. That is, throughout this work, the value of $\delta V_2[q(\cdot),t]$ is nonzero during the increase in system coupling. The latter is specified through the function $g(t)$ chosen to satisfy

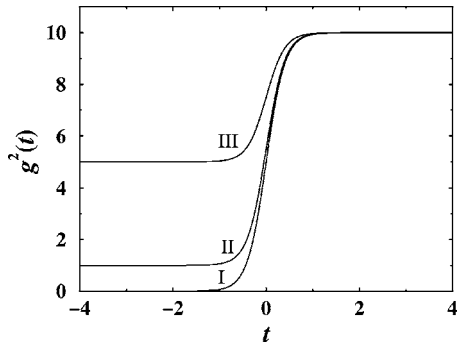

FIG. 1. The square of the irreversible change in the environment $g(t)^2$ is shown here as a function of time for the three cases examined in this study.

$$g(t)^2 = g(-\infty)^2 + \frac{1}{2}[g(\infty)^2 - g(-\infty)^2]\left(1 + \frac{e^{t/\tau_g} - 1}{e^{t/\tau_g} + 1}\right), \tag{12a}$$

as illustrated in Fig. 1, or equivalently as

$$g(t)^2 = \frac{1}{2}[g(\infty)^2 + g(-\infty)^2] + \frac{1}{2}[g(\infty)^2 - g(-\infty)^2]\tanh\left(\frac{t}{2\tau_g}\right). \tag{12b}$$

A. Coupling constants

The values of the coupling constants in Eq. (6) can be obtained from the reverse cosine transform of Eq. (14),

$$\frac{c_i^2}{\omega_i^2} = \frac{2\omega_c}{\pi}\int_0^\infty dt\,\cos(\omega_i t)\,\gamma_0 e^{-t/\tau}, \tag{13}$$

such that an effective (discretized) friction kernel of the form

$$\gamma_0(t) = \sum_{i=1}^{N} \frac{c_i^2}{\omega_i^2}\cos(\omega_i t), \tag{14}$$

is used to approximate $\gamma_0 e^{-t/\tau}$. The coupling constants c_i in Eq. (6a) are readily obtained on a discrete (and finite) grid of N nontrivial frequencies, $\omega_i \equiv i\omega_c$, by equating the spectral densities of the exponential friction to that of discretization. The smallest frequency $\omega_c \equiv 1/(M\tau)$ can be characterized in terms of the characteristic integer M which effectively sets the longest time scale that can be measured before false recurrences appear due to the discretization. The coefficients can be written (as, for example, also obtained by Topaler and Makri[51]) as

$$c_i = \sqrt{\left(\frac{2\gamma_0\tau\omega_c}{\pi}\right)\left(\frac{\omega_i^2}{1+\omega_i^2\tau^2}\right)}. \tag{15}$$

$1/(N\omega_c)$ represents the shortest time scale of interest. This connection between the continuum stationary friction kernel and the discrete number of frequencies and coupling strengths [Eq. (14)] is exact in the continuum limit ($N\to\infty$). However, M must also be large enough so as to ensure the decay in correlations between the bath modes, typically $M \geqslant 4$. Simulations of the GLE (with constant friction) were performed to confirm a suitable number of bath particles for which convergence of the relationship in Eq. (14) was observed. It was found that as few as 20 harmonic bath modes can yield acceptable convergence of the velocity correlation function of the chosen coordinate because its decay is much faster than the recurrence time in the bath modes. Nonetheless, to ensure that there are enough modes to approximately satisfy the continuum limit at the longest and shortest times of interest while also limiting the requisite computing power, the number of harmonic bath modes, N, used in the present work have been taken to be 200.

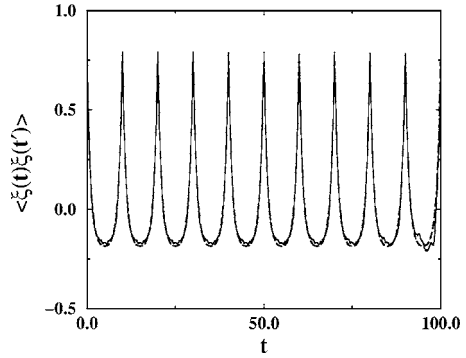

FIG. 2. The average correlation of the random forces on the tagged particle $\langle\xi(t)\xi(t')\rangle$ as a function of time t (solid line) for the GLE case with coupling constants calculated as in Eq. (16). The dashed line represents the friction kernel as calculated in Eq. (14).

Although the coupling constants have been calculated as per Eq. (15) in the simulations of the mechanical projection of the iGLE presented in this work, it is beneficial to examine some other choices of the coupling constants, c_i. The main question is how to best equate the continuum (left hand side) and discrete (right hand side) representations of Eq. (14) in the frequency domain. One alternative method is that of Reese *et al.*,[52] in which the coupling constants are obtained, not by integrating the spectral function over an infinite domain as above, but over a domain bounded by the longest time scale $1/\omega_c'$. The resulting coefficients,

$$c_i = \sqrt{\left(\frac{2}{t_c}\omega_i^2\gamma_0\right)\left[\frac{1/\tau}{\omega_i^2 + 1/\tau^2} + \frac{e^{-t_c/\tau}\omega_i\sin(\omega_i t_c)}{\omega_i^2 + 1/\tau^2}\right]}, \tag{16}$$

are associated with a correspondingly discrete frequency $\omega_i \equiv i\omega_c'$ as before, but the smallest frequency is redefined as $\omega_c' = \pi/(p\tau)$ for some characteristic integer p. The use of the coupling constants of Eq. (16) in the Hamiltonian representation of the GLE yields very close agreement between the friction kernel as specified by Eq. (14) and the correlation function for the random forces on the tagged particle as shown in Fig. 2. Unfortunately, the system still retains a long-time periodicity associated with the mode described by the largest inverse frequency. In an attempt to sidestep this issue, the chosen frequencies in the domain could be selected incommensurably by sampling frequencies randomly within each window, $I_i \equiv (\{i-1\}\omega_c, i\omega_c)$. Given a random sequence of frequencies $\{\omega_i^R\}$ in which $\omega_i^R \in I_i$ for each i, the coefficients can then be reevaluated leading to the result

$$c_i = \sqrt{\left(\frac{2\gamma_0}{\pi}\right)(\omega_i^R)^2[\tanh^{-1}(i\tau\omega_c) + \tanh^{-1}(\{i-1\}\tau\omega_c)]}. \tag{17}$$

This choice of coefficients was also tested on the GLE but it led to similar results for the correlation function of the projected (random) forces $\xi(t)$, both in terms of the accuracy and in reproducing the long-time periodicity. It was therefore determined that the results for the GLE (and thereby the iGLE) are not highly sensitive to the limiting form of the coupling constants so long as the choice satisfies the appropriate friction kernel, while the random choice of frequencies did not remove the false long-time periodicity in the autocorrelation of the force $\xi(t)$.

This discussion, though somewhat pedantic, does offer a critical warning: any numerically measured behavior in the chosen particle that is correlated for times longer than the period of the false long-time periodicity in the discrete representation is suspect to error. This, in turn, places an upper bound on the slowest time scale, viz., t_g in Eq.(12), that can be imposed on the nonstationary behavior of the bath coupling for a given choice of discrete oscillators in the Hamiltonian representation. In the simulations that follow, this bound is indeed satisfied.

B. The particle in a free-particle bare potential

The numerical equivalence between the iGLE and the Hamiltonian system of Eq. (6) can be illustrated using the same model of the nonequilibrium change in the environment originally investigated in the context of the phenomenological iGLE.[31] To this end, numerical results are presented for the Hamiltonian system of a tagged free particle $[V(q)=0]$ bilinearly coupled to a bath of 200 harmonic modes whose smallest characteristic bath frequency is $\omega_c = 1/(M\tau)$, where $M=4$. Individual bath frequencies are taken at discrete values, $\omega_i=(i-1/2)\omega_c$, and coefficients as per Eq. (15). All other parameters have identical values to those used in the numerical integration studies of the iGLE in Ref. 31, with the exception that 100 000 trajectories were used in this study (which is a tenfold increase in the number of trajectories). In summary, all simulations share the following set of parameters: $N=100\,000$, $k_BT=2.0$, $\gamma_0=10.0$, $\tau=0.5$, and $\tau_g = 0.2$. The time-dependent friction is modulated through the switching function $g(t)$, as shown in Fig. 1. The system is propagated using the velocity-Verlet method with smaller time steps ($\Delta t=1\times10^{-4}$ when $t\geq-8$) during the friction switching regime than during the constant friction regime ($\Delta t=1\times10^{-3}$ when $t<-8$).[53] Each individual trajectory is first equilibrated, starting at $t=-20$, to ensure that the observed dynamics are influenced only by the irreversible change in the friction and not the dynamics of equilibration.

In order to determine whether or not the $\delta V_2[q(\cdot),t]$ term is negligible, simulations were first performed with $\delta V_2[q(\cdot),t]=0$. For all three cases of the change in friction, the nonlocal $\delta V_2[q(\cdot),t]$ term was found to be non-negligible as can be seen in Fig. 3 by the fact that the system does not obey equipartition of energy during times near $t=0$. The most dramatic deviations are seen in case I when the switching function, $g(t)$, and consequently the instantaneous friction increases across the largest range. The least dramatic deviation unsurprisingly occurs in case III in which the solvation merely changes from moderate to strong dissipation of the chosen system. It is also evident that the system does not maintain a constant temperature in any of these cases during the nonequilibrium disturbance.

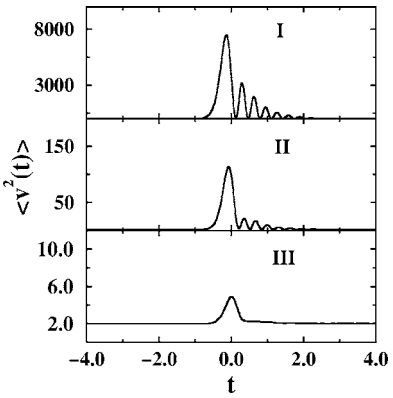

FIG. 3. The mean-square velocity $\langle v^2(t)\rangle$ is displayed for each of the cases as a function of time t and case I, II, or III with the nonlocal term $\delta V_2[q(\cdot),t]$ set equal to zero.

However, upon introducing the nontrivial terms, $\delta V_2[q(\cdot),t]$ and its derivative [Eq. (6c)], within the Hamiltonian equations of motion, equipartition for the system is preserved, as shown in Fig. 4. The $\delta V_2[q(\cdot),t]$ term is therefore not negligible in the extreme test cases examined in this work in which all the interesting time scales, $\sqrt{1/\gamma_0}$, t_g, and τ, are comparable. As can be further seen from Fig. 4, all three test cases lead to the same level of fluctuations in the long-time regime even though they begin at different initial macroscopic states. In the limit of an infinite number of trajectories, all cases would exhibit no fluctuations as they would be suppressed by the averaging process. The fluctuations observed here, due to finite-size effects, are indicative of the system dynamics. For example, in case I the particle obeys equipartition perfectly for the early regime because its motion is ballistic, whereas the early time dynamics for cases II and III clearly show the influence of coupling to the harmonic bath particles. It can be seen from the plot of the

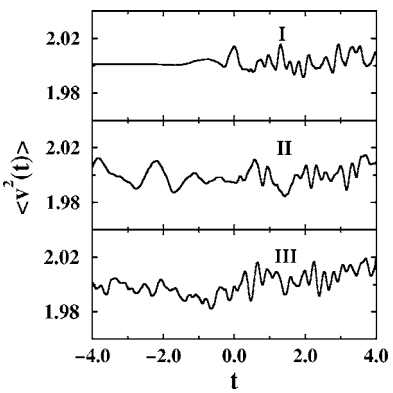

FIG. 4. The mean-square velocity $\langle v^2(t)\rangle$ is displayed for each of the cases as a function of time t and case I, II, or III with the nonlocal term $\delta V_2[q(\cdot),t]$ explicitly considered.

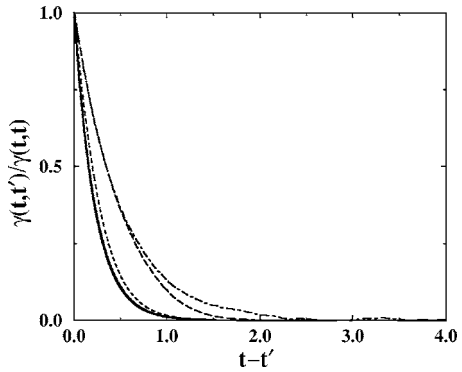

FIG. 5. The normalized nonstationary friction kernel, $\gamma(t,t')/\gamma(t,t)$, in case I at several different times t (−4.0, thick solid line, −0.5, solid line; 0.0, dashed line, 1.0, long-dashed line; and 4.0, dot-dashed line) as a function of the previous times $t-t'$. In each case, the force correlation function $\langle\xi(t)\xi(t')\rangle/\langle\xi(t)\xi(t)\rangle$ is also plotted using the same dashing, but is indistinguishable from the corresponding normalized friction kernel.

average square velocity that the system conserves energy in these calculations when the $\delta V_2[q(\cdot),t]$ term is included.

The construction of the iGLE also requires that the correlation function of the random forces satisfies a nonstationary extension of the FDR,

$$k_B T g(t) g(t') \gamma_0(t-t') = \langle \xi(t)\xi(t')\rangle, \tag{18}$$

with respect to the explicit forces $\xi(t)$ on the tagged particle seen in a microscopic system,

$$\xi(t) = \dot{v} + \gamma_0 g(t) \int_0^t dt' g(t') \gamma_0(t-t') v(t') - F(t). \tag{19}$$

That the mechanical system satisfies this relationship is illustrated in Figs. 5–7 for cases I–III, respectively. In all of these figures, both the force correlation functions and the nonstationary friction kernel are overlayed exactly for each of the cases and times displayed. The integral can be simplified using an auxiliary variable z_2 akin to the method for replacing $\delta V_2[q(\cdot),t]$ with z. The auxiliary variable satisfies

$$\frac{\partial z_2}{\partial t} = \dot{g}(t) v(t) - \frac{1}{\tau} z_2(t). \tag{20}$$

The explicit expression for the forces on the tagged particle can then be obtained at each time step by substitution,

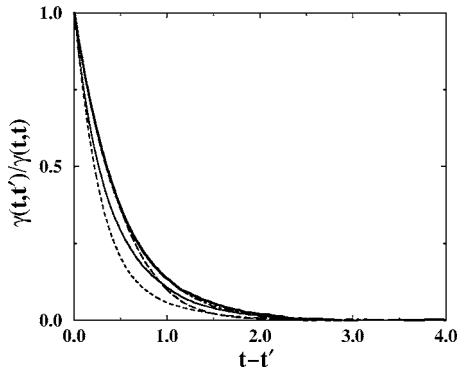

FIG. 6. The nonstationary friction kernels $\gamma(t,t')$ and force correlation functions in case II are plotted as in Fig. 5.

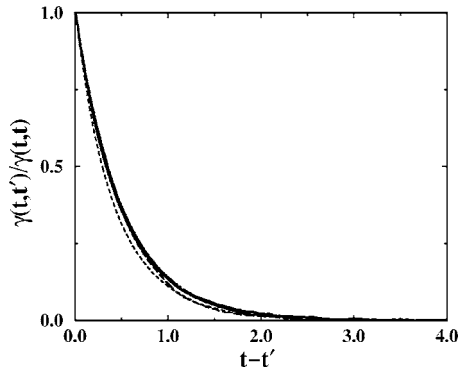

FIG. 7. The nonstationary friction kernels $\gamma(t,t')$ and force correlation functions in case III are plotted as in Fig. 5.

$$\xi(t) = \dot{v} + \gamma_0 g(t) z_2(t) - F(t). \tag{21}$$

The autocorrelation function of the force due to the bath, viz., the random force in the projected variables, obey the FDR for all cases and times. It should be emphasized that both this observation and the remarkable agreement between all the figures and those obtained for the corresponding iGLE in Ref. 31 would not have been found if the nonlocal term were omitted.

The velocity autocorrelation functions for the tagged free particle are shown in Fig. 8. At the origin ($t-t'=0$), each of the autocorrelation function reduces to the equilibrium average, $\langle v(t)^2\rangle$, and take on a value near 2.0, satisfying equipartition. That is, the autocorrelation functions match the previous results exactly with the exception that the case I curves were mislabeled in Fig. 5 of Ref. 31, and the present work serves to correct the misprint. The long-time ($t=4.0$) autocorrelation functions are all the same, indicating that all cases reach the same equilibrium, as would be expected. In case I, the early time ($t=-4.0$) autocorrelation function is a straight line because the particles are in the ballistic regime therein, as will be discussed in more detail in Sec. III C. Thus the dynamics of the chosen coordinate evolves in the same manner as seen in the previous studies integrating the phenomenological iGLE.

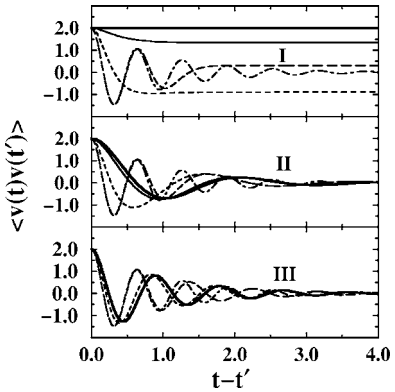

FIG. 8. The velocity autocorrelation function of the free tagged particle, $\langle v(t)v(t')\rangle$, is displayed for each of the three cases of the change in friction at initial times t (−4.0, thick solid line; −0.5, solid line; 0.0, dashed line; 1.0, long-dashed line; and 4.0 dot-dashed line). The panels indicate cases I–III from top to bottom.

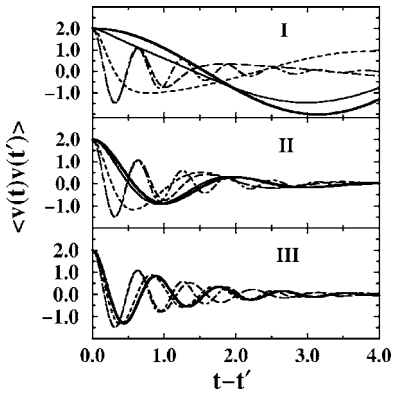

FIG. 9. The velocity autocorrelation function of the harmonic tagged particle, $\langle v(t)v(t')\rangle$, is displayed using the same symbols as in Fig. 8.

C. The particle in a harmonic bare potential

A possibly different set of dynamics might be observed if the chosen particle's bare potential is trapped by a harmonic bare potential. In order to explore this issue, various simulations of the mechanical system were undertaken using the same set of conditions investigated in the free-particle case of Sec. III B. The only additional parameter required to specify this system is the harmonic frequency, $\omega=1$, of the bare potential. Perhaps surprisingly, the numerical integration of this system exhibits similar convergence properties as in the free-particle case with the following exceptions: The system with the tagged particle in a harmonic well is less sensitive to the increase in friction and can be simulated accurately with larger time steps than the free-particle case due to the confinement imposed by the harmonic well. The harmonic system does not yield the large spikes in the average square velocity seen in the free-particle case when the $\delta V_2[q(\cdot),t]$ is ignored (by setting it to zero). The explicit calculation of $\delta V_2[q(\cdot),t]$ to propagate the trajectories is still a necessity for accurate and converged results.

The comparison between the autocorrelation functions for the free and harmonic particles in Figs. 8 and 9, respectively, is instructive. The main differences between them appear when the earlier time t' occurs at a time t^* before $g(\cdot)$ has started to change, i.e., earlier than ca. $t^*\approx -1$. Recall that the initial condition at very early times ($t=-20$) of the trajectories has been taken to be that in which all the particle energy has been placed into the kinetic term. (This initial condition is only visible in the ballistic regime. Otherwise the bath is sufficiently large and the trajectories are propagated sufficiently long that the subsystem effectively equilibrates before the particle reaches the interaction region displayed here.) Because the particles move ballistically until t^*, the correlation function reduces to $\langle v(t)v(t')\rangle \approx \langle v(t)v(t^*)\rangle$ for $t'<t^*$. In the early time case where $t(=-4)$ is also less than t^*, the correlation function reduces to the equipartition average $\langle v(t^*)^2\rangle = k_BT$. Otherwise, it is simply a constant for $t'<t^*$ as seen in case I of Fig. 8. The deterministic regime also plays a role in the sinusoidal shapes of case I of Fig. 9. The only difference is that the deterministic dynamics of the harmonic oscillator leads to a solution of the velocity that is sinusoidal with the frequency ν specified by the harmonic potential. Thus for $t'<t^*$, the velocity is not constant, but rather equal to $v(t^*)\cos[\nu(t^*-t')]$. Consequently the velocity autocorrelation functions reduce to a sinusoidal wave for $t'<t^*$ in case I of Fig. 9.

Why do the remaining autocorrelation functions between the free- and harmonic particle cases look so similar? As is evident from panel I in Fig. 9, the frequency of the harmonic oscillator is smaller than that induced by the bath in the final friction regime. Hence, once the bath begins to interact strongly with either the free or harmonic particles, it adds an effective contribution to the free energy, the $\delta V_1(q,t)$ term in Eq. (6a), that is larger than $V(q)$ and therefore dominates the forces on the particles. That is, though the initial bare potentials used in the two cases studied here appear rather different, they lead to essentially the same potential of mean force because the bare potentials are dominated by the mean-field interactions between the particle and the bath. The fact that the nonstationary mechanical system exhibits this behavior correctly might not have been *a priori* obvious.

IV. CONCLUDING REMARKS

The equivalence of the stochastic iGLE and the nonstationary mechanical system, i.e., the fact that the higher-order corrections in the projection of the latter into the former are negligible, has been demonstrated by numerical integration of the equations of motion corresponding to the Hamiltonian in Eq. (6). Two different (though simple) extremes were considered for the dynamics of the chosen particle in which the bare potential is represented either as a free-particle or a bound harmonic oscillator. The numerical agreement in the observables and two-point correlation functions between the mechanical system and its projection under each of these potentials is well within the point size of the figures when only 200 explicit bath particles is used in the former. Although a systematic study of the minimum required number of bath particles has not been explicitly shown, the use of fewer bath particles did not produce as good agreement because they were unable to simultaneously capture the minimum short time step needed to describe the motion of the chosen particle and the minimum long time step needed for the nonstationary system to retain memory of the past behavior. It should be emphasized that the agreement is contingent upon the explicit inclusion of the nonlocal dissipative term which is nonzero for all the cases of interest in this study.

The deterministic mechanical system serves as further evidence that the stochastic equation of motion, viz., the iGLE, is not purely fiction (e.g., phenomenological), but rather is equivalent to a physical open system with an explicit energy function or Hamiltonian in which the coupling between the chosen particle and the bath is driven parametrically (externally). This system can be closed by way of an explicit equation of motion describing the parametric dependence. The present results also suggest that the nonequilibrium dynamics of a chosen particle in a *nonequilibrium* bath can be characterized mechanistically through a uniform time-dependent mean-field coupling to all of the bath modes.

It should now be possible to calculate the work done on the system by way of an external driving term under nonequilibrium conditions. Comparison of this work to the free-

energy differences between the specified initial and final states could provide an additional test to the Jarzynski inequality, and will be pursued in future work.[9,15]

Though the connection between the nonlocal mechanical system and the projected nonstationary system has been shown here, it might not convince the reader who doubts that real solvent environments can be described by harmonic baths let alone harmonic baths with nonlocal terms. The former is the well-known case of the GLE and the argument in its favor is similar to that of the nonlocal mechanical system. Namely, the mechanical system is one possible construct whose projection satisfies the phenomenological equations of motion. Its primary use is thus the demonstration of the existence of such constructs and in the calculation of observables in the projected variables. (A secondary use has been in the interpretation of the details of the environment's behavior, but such practice has not been universally accepted.) The fact that such a construct is possible for the nonstationary phenomenological representation (iGLE) suggests that the latter may indeed be recoverable (by way of projections) from more general atomistic or molecular models. Indeed, in an unpublished work, the diffusion dynamics of a hard-sphere particle through a nonequilibrium colloidal suspension has been surmised by an iGLE-type model.[41]

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[1] D. Chandler, *Introduction to Modern Statistical Mechanics* (Oxford, New York, 1987).
[2] R. Zwanzig, *Nonequilibrium Statistical Mechanics* (Oxford University Press, London, 2001).
[3] P. W. Anderson, Science **177**, 393 (1972).
[4] N. Goldenfeld and L. P. Kadanoff, Science **284**, 87 (1999).
[5] G. M. Whitesides and B. Grzybowski, Science **295**, 2418 (2002).
[6] G. M. Whitesides and R. F. Ismagilov, Science **284**, 89 (1999).
[7] A. I. Frenkel, C. W. Hills, and R. G. Nuzzo, J. Phys. Chem. B **105**, 12689 (2001).
[8] J. Buceta and K. Lindenberg, Phys. Rev. E **66**, 046202 (2002).
[9] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[10] G. Gallavotti, Chaos **8**, 384 (1998).
[11] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).
[12] D. J. Searles and D. J. Evans, J. Chem. Phys. **112**, 9727 (2000).
[13] D. J. Searles and D. J. Evans, J. Chem. Phys. **113**, 3503 (2000).
[14] P. Gaspard, J. Chem. Phys. **120**, 8898 (2004).
[15] C. Jarzynski, J. Stat. Mech.: Theory Exp. 2004, P09005.
[16] H. A. Kramers, Physica (Utrecht) **7**, 284 (1940).
[17] R. Zwanzig, J. Chem. Phys. **33**, 1338 (1960).
[18] R. Zwanzig, *Statistical Mechanics of Irreversibility* (Wiley-Interscience, New York, 1961), Vol. 3, pp. 106–141.
[19] I. Prigogine and P. Resibois, Physica **27**, 629 (1961).
[20] G. W. Ford, M. Kac, and P. Mazur, J. Math. Phys. **6**, 504 (1965).
[21] H. Mori, Prog. Theor. Phys. **33**, 423 (1965).
[22] R. Kubo, Rep. Prog. Phys. **29**, 255 (1966).
[23] J. T. Hynes, *The Theory of Reactions in Solution* (CRC, Boca Raton, FL, 1985), Vol. 4, pp. 171–234.
[24] J. T. Hynes, Annu. Rev. Phys. Chem. **36**, 573 (1985).
[25] A. Nitzan, Adv. Chem. Phys. **70**, 489 (1988).
[26] B. J. Berne, M. Borkovec, and J. E. Straub, J. Phys. Chem. **92**, 3711 (1988).
[27] P. Hänggi, P. Talkner, and M. Borkovec, Rev. Mod. Phys. **62**, 251 (1990), and references therein.
[28] S. C. Tucker, M. E. Tuckerman, B. J. Berne, and E. Pollak, J. Chem. Phys. **95**, 5809 (1991).
[29] S. C. Tucker, J. Phys. Chem. **97**, 1596 (1993).
[30] E. Pollak, *Theory of Activated Rate Processes* (Marcel Dekker, New York, 1996), pp. 617–669.
[31] R. Hernandez and F. L. Somer, J. Phys. Chem. B **103**, 1064 (1999).
[32] R. Hernandez and F. L. Somer, J. Phys. Chem. B **103**, 1070 (1999).
[33] F. L. Somer and R. Hernandez, J. Phys. Chem. A **103**, 11004 (1999).
[34] F. L. Somer and R. Hernandez, J. Phys. Chem. A **104**, 3456 (2000).
[35] R. Hernandez, J. Chem. Phys. **111**, 7701 (1999).
[36] R. Hernandez and F. L. Somer, *Nonstationary Stochastic Dynamics and Applications to Chemical Physics* (Kluwer Academic, The Netherlands, 2000), pp. 91–116.
[37] C. R. Locker and R. Hernandez, Proc. Natl. Acad. Sci. U.S.A. **98**, 9074 (2001).
[38] A. N. Drozdov and S. C. Tucker, J. Phys. Chem. B **105**, 6675 (2001).
[39] E. Hershkovitz and R. Hernandez, J. Chem. Phys. **122**, 014509 (2005).
[40] C. D. Jones and L. A. Lyon, Macromolecules **36**, 1988 (2003).
[41] A. V. Popov, J. Melvin, and R. Hernandez (unpublished).
[42] A. O. Caldeira and A. J. Leggett, Phys. Rev. Lett. **46**, 211 (1981), Ann. Phys. (N.Y.) **149**, 374 (1983).
[43] B. J. Gertner, J. P. Bergsma, K. R. Wilson, S. Lee, and J. T. Hynes, J. Chem. Phys. **86**, 1377 (1987).
[44] E. Pollak, J. Chem. Phys. **86**, 3944 (1987).
[45] K. Lindenberg and V. Seshadri, Physica A **109A**, 483 (1981).
[46] K. Lindenberg and E. Cortés, Physica A **126A**, 489 (1984).
[47] B. Carmeli and A. Nitzan, Chem. Phys. Lett. **102**, 517 (1983).
[48] R. Zwanzig, J. Stat. Phys. **9**, 215 (1973).
[49] E. Cortés, B. J. West, and K. Lindenberg, J. Chem. Phys. **82**, 2708 (1985).
[50] E. Pollak, J. Chem. Phys. **85**, 865 (1986).
[51] M. Topaler and N. Makri, J. Chem. Phys. **101**, 7500 (1994).
[52] S. Reese, S. Tucker, and G. Schenter, J. Chem. Phys. **102**, 104 (1995).
[53] M. P. Allen and D. J. Tildesley, *Computer Simulations of Liquids* (Oxford, New York, 1987).